

1st, the chemical composition of the liquid; 2nd, the kind of positive metal; 3rd, to a less degree with the kind of negative metal; 4th, the temperature at the surface of the positive metal, and at that of the negative one; and 5th, with the kind of galvanometer employed.

The order of the degree of sensitiveness or magnitude of the "minimum-point" is manifestly related to that of degree of chemical energy of the liquid, and, therefore, also to the atomic and molecular weights of the dissolved substances, and to the ordinary chemical groups of halogens. With certain exceptions, it is also distinctly related to the amounts of chemical heat. The greater the degree of free chemical energy of the dissolved substance, and the greater its action upon the positive metal, the smaller the proportion of it required to upset the balance. The proportion necessary for this purpose probably represents a fixed amount of voltaic energy in all cases, viz., the amount necessary to overcome the mechanical inertia of the needle of the particular galvanometer employed.

As the "minimum-point" of a chemically active substance dissolved in water is usually much altered by adding almost any soluble substance to the mixture, measurements of that point in a number of liquids at a given temperature with the same voltaic pair and galvanometer, will probably throw some light upon the state of combination and degree of chemical freedom of substances dissolved in water.

## II. "On the Change of Potential of a Voltaic Couple by Variation of Strength of its Liquid." By G. GORE, F.R.S. Received May 31, 1888.

Having found a thermo-electric pile (see 'Birmingham Phil. Soc. Proc.,' vol. 4, p. 130) convenient in detecting and measuring small changes of voltaic potential ('Roy. Soc. Proc.,' May 3rd, 1888), I have taken advantage of that circumstance to measure by the method of balance the above phenomenon in various liquids.

The following are a few examples of measurements thus made of the influence of varying quantities of different substances upon the electromotive force of a voltaic couple composed of zinc and platinum immersed in distilled water :—

Table I.— $\text{KClO}_3$  in 465 grains of Water at  $16^\circ \text{C}$ .

Grains.	Volts.	Grains.	Volts.
39	1·0228	18	1·0171
36	"	15	1·0142
33	"	12	1·0056
30	"	9	0·9999
27	"	6	0·9828
24	"	3	0·9282
21	"		

The strongest of the above solutions was a saturated one.

Table II.—Ditto at  $10^\circ \text{C}$ .

Grains.	Volts.	Grains.	Volts.
3	0·9282	2·1	0·9170
2·7	0·9227	1·8	0·9084
2·4	0·9198	Water alone.	"

The electromotive force gradually increased with the strength of the solution until 21 grains of the salt had been added; it then remained uniform up to the point of saturation. The total increase of electromotive force was 0·1144 volt. The smallest proportion of salt required to upset the balance of the couple was 1 part in between 221 and 258 parts of water.

Table III.— $\text{KCl}$  in 465 grains of water at  $12^\circ \text{C}$ .

Grains.	Volts.	Grains.	Volts.
147	1·15436	57	1·15436
129	"	39	"
111	"	21	"
93	"	3	"
75	"		

The strongest of these solutions was saturated with the salt.

Table IV.—Ditto at 8° C.

Grains.	Volts.	Grains.	Volts.
0·003	1·1546	0·001001	1·0228
0·002667	1·1171	0·000669	0·9942
0·002334	1·0543	0·000336	0·937
0·002001	1·0943	0·000224	„
0·001668	1·080	0·000112	„
0·001335	1·0514	Water.	„

The electromotive force gradually increased with the strength of the solution up to 0·002 grain of the salt, then decreased, and afterwards increased again up to 0·003 grain, and then remained constant until the saturation point was attained. The total increase of electromotive force was 0·21736 volt. The minimum proportion of chloride necessary to upset the balance of potential of the couple lay between 1 part in 695,067 and 1,390,134 parts.

Table V.—HCl in 465 grains of Water at 16·5° C.

Grains.	Volts.	Grains.	Volts.
0·15	1·3487	0·05628	1·1715
0·1407	1·2945	0·04691	„
0·1313	1·2459	0·03754	1·1658
0·1219	1·2373	0·02816	1·1515
0·1125	1·1915	0·01879	1·1429
0·10314	1·1615	0·00942	1·1286
0·09377	„		
0·0844	„	0·00005	1·0228
0·07502	„	0·0000474	0·9799
0·06565	„	Water.	„

The electromotive force increased gradually with the strength of the solution up to 0·06565 grain of the anhydrous acid, then remained constant until 0·10314 grain had been added, and then increased up to the strongest solution employed. The total increase of electromotive force was 0·3688 volt. The smallest proportion of the anhydrous acid required to disturb the balance of the couple lay between 1 part in 9,300,000 and 9,388,185 parts of water.

Table VI.—Bromine in 465 grains of Water at 12·5° C.

Grains.	Volts.	Grains.	Volts.
20·10	1·9746	9·84	1·9089
18·39	1·9603	8·13	1·8974
16·68	1·9517	6·42	1·8775
14·97	1·9403	4·71	1·8715
13·26	1·9317	3·00	1·8743
11·55	1·9203		

The strongest of these solutions was a saturated one. The electro-motive force first decreased and then increased almost regularly with the strength of the liquid up to the saturation point. The total amount of increase was 0·13 volt.

Table VII.—Ditto at 16° C.

Grains.	Volts.	Grains.	Volts.
3·0	1·8746	1·5	1·7400
2·85	1·8173	1·35	„
2·7	1·7973	1·2	„
2·55	1·7887	1·05	1·7229
2·4	1·7687	0·9	1·7200
2·25	1·7573	0·75	1·7172
2·1	„	0·6	1·7027
1·95	1·7458	0·45	„
1·8	„	0·3	„
1·65	„	0·15	„

By gradually increasing the strength of the liquid, the electro-motive force at first remained uniform, then increased, remained uniform again, then gradually increased, finally at a rapid rate. The total increase was 0·1719 volt.

Table VIII.—Ditto at 13·7° C.

Grains.	Volts.	Grains.	Volts.
0·0004	1·2888	0·0001235	1·1653
0·0003605	„	0·000084	1·1515
0·000321	1·2802	0·0000445	1·1086
0·0002815	1·2745		
0·000242	1·2459	0·0000081	0·937
0·0002025	1·2316	0·000005	0·9084
0·000163	1·1944	Water.	„

By regularly increasing the strength of the solution, the electromotive force at first increased very rapidly, then with decreasing rapidity, and finally remained uniform. The total increase was 0.38 volt. The smallest proportion of bromine required to upset the balance lay between 1 in 77,500,000 and 84,545,000 parts of water.

With each of these substances, and with all others which I have examined, a gradual and regular increase of strength of the solution from the weakest up to a saturated one, was attended by a more or less irregular change of electromotive force.

By plotting the quantities of dissolved substance as ordinates to the electromotive forces as abscissæ, each substance or mixture of substances in every case yielded a different curve of variation of electromotive force by uniformly changing the strength of its solution. With a given voltaic couple at a given temperature, the curve was constant and characteristic of the substance. As the least addition of a soluble foreign substance greatly changed the "minimum-point," and altered the curve of variation of potential, both the curve and the minimum proportion of a substance required to upset the voltaic balance may probably be used as tests of the chemical composition of the substance, and as means of examining its state of combination when dissolved. By varying the strength of the solution at each of the metals separately, a curve of change of potential was obtained for each positive metal, but not for every negative one.

### III. "Influence of the Chemical Energy of Electrolytes upon the 'Minimum Point' and Change of Potential of a Voltaic Couple in Water." By G. GORE, F.R.S. Received June 7, 1888.

In a communication to the Royal Society, May 3rd, 1888, on "The Effect of Chlorine upon the Electromotive Force of a Voltaic Couple," and in a subsequent one on "The Minimum Point of Change of Potential of a Voltaic Couple," I have shown that by opposing to each other two currents of equal electromotive force from two perfectly similar couples of magnesium-platinum or zinc-platinum in distilled water, and gradually adding to one of the cells sufficiently minute quantities of a suitable substance, such as chlorine, hydrochloric acid, or a soluble salt, &c., the voltaic balance is not disturbed until a certain definite proportion of the substance has been added, and that the proportion required to be added is excessively small (about 1 in 17,000 millions) in the case of chlorine